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Sertifikaat

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Application forms P.1, P.2, provisional specification and drawings of South African Patent Application 2004/0082 as originally filed in the Republic of South Africa on 7 January 2004 in the name of HYDROMET (PTY) LTD for an invention entitled: "EXOTHERMIC PRESSURE LEACH AUTOCLAVE CIRCUITS."

Geteken te in die Republiek van Suid-Afrika, hierdie dag van
Signed at PRETORIA in the Republic of South Africa, this 19th day of September 2005

Registrateur van Patente
Registrar of Patent

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978

(IN DUPLICATE) **Form P1**

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REGISTRATEUR VAN PATENTE, MODELLE, HANDELSMERKE EN OUTEURSREG

07-Jan-2004

APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT

The grant of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

21 01 OFFICIAL APPLICATION No. 2004/0082	LF & Co. Ref: ZA.P.2306
71 APPLICANT/S (Full Name/s) HYDROMET (PTY) LTD	
ADDRESS/ES OF APPLICANT/S 20 Womble Street, Rowhill, Springs, 1559	
59 TITLE OF INVENTION EXOTHERMIC PRESSURE LEACH AUTOCLAVE CIRCUITS	

		Country	Number	Date
	Priority is claimed as set out on Form P2. Earliest Priority claimed is:			
	This application if for a Patent Of Addition to patent application No.:	21 | 01		
	This application is a fresh application in terms of Section 37 based on application No.:	21 | 01		

THIS APPLICATION IS ACCOMPANIED BY:

X	1a	A single copy of a provisional application. Number of pages	13	
	1b	Two copies of a complete specification. Number of pages		
X	2	Drawings. Number of sheets	3	formal / informal
	3	Publication particulars and abstract (Form P8 in duplicate)		
	4	Two copies of the drawing for the abstract. Figure No.		
	5	An assignment of invention		
	6	Certified priority documents. Numbers		
	7	Translation/s of the priority document/s		
	8	An assignment of priority rights		
	9	A copy of Form P2 and specification of ZA Patent Application No/s.	21 | 01	
	10	A declaration and power of attorney on Form P3		
	11	Request for ante-dating on Form P4		
	12	Request for Delay of Acceptance on Form P4		
X	13	Form P2 plus copy		

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DATE **07-Jan-2004**

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71 Applicants substituted:	Date registered

71 Assignee(s):	

72 Full name(s) of inventor(s):

GRENVIL, Marquis Dunn

PRIORITY CLAIMED	33	Country	31	Number	32	Date

54 Title of Invention

EXOTHERMIC PRESSURE LEACH AUTOCLAVE CIRCUITS

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61 Patent of Addition No.	Date of any Change
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Form P6

REPUBLIC OF SOUTH AFRICA
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PROVISIONAL SPECIFICATION

(Section 30(1) - Regulation 27

21	01 Official Application No.	22	Filing Date				LF & Co. Ref:
2004/0082		07-Jan-2004				ZA.P.2306	

71	APPLICANT/S (Full Name/s)
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	GRENVIL, Marquis Dunn
54	**TITLE OF INVENTION**
	EXOTHERMIC PRESSURE LEACH AUTOCLAVE CIRCUITS

EXOTHERMIC PRESSURE LEACH AUTOCLAVE CIRCUITS

TECHNICAL FIELD:

This invention relates to exothermic pressure leach autoclave circuits and is concerned primarily, though not exclusively, with improving the capacity or throughput of existing circuits.

BACKGROUND ART:

Pressure leach autoclave circuits are employed in the leaching of ores, concentrates, mattes, alloys, intermediates and the like for the recovery of metals into solution. Once the metals are extracted into solution the value metals can be recovered by hydrometallurgical means, such as purification followed by electrowinning, pyrohydrolysis, crystallisation, hydrogen reduction and other unit operations. In many of these integrated flowsheets (refer to Figure 1) the pressure leach step is pivotal to the recovery of the value metals from the host material.

The leaching is often accompanied by the release of energy that has to be removed in order to avoid exceeding the design operating temperatures of the autoclave vessel. For example, in the leaching of millerite produced by the action of hydrogen sulphide gas on a neutralised leachate sourced from a laterite pressure acid leach circuit the reaction could be represented by: $NiS + 4O \Longrightarrow NiSO_4 + \text{heat}$. The heat release for this reaction as calculated from heats of formation at 25°C is approximately 189 kilocalories per g mole. The release of this energy from a 15 to 17% feed slurry could produce temperatures in excess of 200°C within the autoclave, whereas the normal operating temperature should be 160°C at a pressure of 1200 kPa(g) for example. Frequently most of this energy is liberated in the first compartment, with smaller quantities only being generated in the downstream compartments. While this large amount of heat is used in process steps such as to raise the feed slurry to the design operating temperature, in many systems the design operating temperature can be exceeded in the first compartment.

The excess heat could be removed by a variety of means, such as quenching by introducing a cooling fluid into the autoclave, internal cooling coils, external coolers, and flash and recycle. Quenching and internal coils have many known practical and process limitations. External coolers avoid many of the problems of internal coils but still may result in the introduction of a larger feed mass, reduction of reaction extent in the first compartment and consequent extra heat load in the second and ensuing compartments. Unless design flexibility is provided, the temperatures can `run away' and unleached product can be discharged from the autoclave.

The flash and recycle system was first introduced by the current inventor in the mid 1980's and employs a first autoclave compartment flash via a flash tank with flash underflow return to the autoclave feed tank. The flash tank serves a dual role; it is both an autoclave feed tank and an external extension of the autoclave's first compartment. In a well designed system, the temperature in the first compartment can be maintained at set point +2°C / -1°C. This temperature control is acceptable for both brick lined and alloy autoclaves. Some of the advantages of this system include: optimal utilisation of the installed reactor volume; concentration of the reactor contents through the evaporation of water flashed as steam; and potential to use the flashed steam as an energy source elsewhere in the operation. Considered holistically the flash and recycle process provides the autoclave designer with the maximum degrees of freedom and several process benefits.

This invention seeks to enhance the benefits of the flash and recycle system.

DISCLOSURE OF THE INVENTION:

One aspect of the invention provides a method of leach autoclave processing including the steps, in a desired order, of:

- -- flashing the autoclave and generating a flash underflow;
- -- performing a solid-liquid separation on the flash underflow to produce a solids fraction and an aqueous fraction; and
- -- returning at least a portion of the solids fraction to the autoclave.

The autoclave may have several compartments, the autoclave flash being obtained from any desired compartment.

Preferably all of the solids fraction is returned to the autoclave. The solids fraction may be returned to any desired compartment of the autoclave. The return to the autoclave may be direct or indirect through any process upstream of the autoclave.

Where the flash is from the first compartment of the autoclave, then preferably the reaction extent in the first compartment is in excess of 50%, more preferably in the range of 90 to 95%.

The solids fraction from the separation may be returned to an autoclave feed tank to be further leached. This is done to increase the autoclave retention times with respect to the solids fraction.

The solids fraction may be returned to an autoclave feed surge tank upstream of the autoclave feed tank or to an autoclave feed density adjust tank between the surge and autoclave feed tank.

The autoclave agitators are preferably operated such that they do not limit mass transfer within the autoclave. Instead mass transfer is preferably controlled by the flash recycle rate.

Preferably the temperature within the first compartment is maintained at set point +2°C / -1°C.

Preferably the method includes adjusting the level of the feed tank to compensate for poor density adjustment in the vessels before the feed tank. This step ensures that out of specification leach product does not pass out of the autoclave.

The solid-liquid separation is often best achieved with a thickener, but it can just as easily be achieved with other means such as a classifier or a filtration step.

A development of the method includes flashing selected subsequent compartments after the first compartment, the flash slurry obtained thereby being fed to a thickener/filtration step.

Preferably the flash underflow from the selected subsequent compartments is

fed to a thickener or a filter, the thickener overflow or filtrate being fed forwards in the process.

The thickener underflow or filter residues may be returned to the autoclave for further processing at the same or different conditions to those prevailing in the initial part of the autoclave. This enables the use a reactor in which two or more similar processes are conducted within the same pressure envelope with only the compartment dividing walls keeping the processes separate.

The thickener overflows or filtrate may be returned to the autoclave for the removal of impurities.

At least a portion, and preferably the whole of, the aqueous fraction in part may be passed to an autoclave discharge tank.

A further development provides that the flash recycle process of the method is employed to leach iron based alloys that contain predetermined quantities of at least one of carbon, sulphur, arsenic, phosphorus and copper.

Preferably, in the further development, the first compartment autoclave conditions are selected to ensure copper is leached in an exothermic process along with the iron and other value metals.

The further development may include the step of establishing a first compartment flash recycle to the feed tank in order to abstract heat and maintain the desired temperature profile in the autoclave.

Preferably slurry obtained from the flash recycle is returned to the feed tank and or preceding density adjust tanks in such a manner as to ensure sufficient soluble copper is present in the feed tank slurry to avoid the formation of dangerous gases, such as hydrogen, hydrogen sulphide, arsine, phosphine and the like.

Preferably the method includes returning the slurry to the feed tank at autoclave temperatures, flashing the slurry down to ambient pressure to release steam, and using the steam to scavenge or sweep out any undesirable

gases that develop from reactions in the autoclave. For example, acetylene developed from contact with the sulphuric acid lixiviant.

Preferably flashed steam generated in the feed or density adjust tanks is also used to flush out undesirable gases that may form as a consequence of non-steady state conditions developing within the process tanks.

Another aspect of the invention provides a leach autoclave processing plant comprising: an autoclave; a flash tank to accept flash from the autoclave and generate a flash underflow; means to return the flash underflow to the autoclave; and separation means to perform a solid-liquid separation on the flash from the autoclave.

Preferably the plant is arranged such that the flash underflow is fed to the separation means and the solids fraction obtained from the separation means is fed to the autoclave.

Further features of the plant of the invention are provided to perform the aspects, developments and steps of the method of the invention described above. Such features may be abstracted from the description of the method and/or from the description and examples below.

Further features, variants and/or advantages of the invention will emerge from the following non-limiting description of examples of the invention made with reference to the accompanying schematic drawings.

BRIEF DESCRIPTION OF THE DRAWINGS:

Figure 1 shows a flow diagram of flash thickener recycle process of the invention;

Figure 2 shows a flow diagram of another flash thickener recycle process of the invention; and

Figure 3 shows a flow diagram of yet another flash thickener recycle process for the leaching of alloys.

DESCRIPTION OF ILLUSTRATED EMBODIMENTS:

In the drawings the same or similar parts have the same reference numbers.

Figure 3 shows a part of a copper concentrate leach plant 10 illustrating a flash recycle thickener process of the invention. The plant includes a density adjust tank 12, an autoclave feed tank 14, a four compartment autoclave 16, an autoclave discharge tank 18, a flash tank 20, and a solid-liquid separation tank 22 in the form of a thickener. Feed lines are indicated with numbers in circles.

Density adjust tank 12 receives a sulphide concentrate, matte or alloy. The density can be adjusted with water (3) and an acid stream (4) such as a spent electrolyte - or an alkali stream such as ammonia, sodium hydroxide, etc. The mass feed to the autoclave feed tank 14 is determined by appropriate instrumentation in the feed line (2).

Feed tank 14 can receive process water (7) if the impact of the flash (5) needs to be compensated for. Alternatively, the use of process water is invoked on a "need-to-have" basis. The feed tank may also receives (6) a reagent, such as sulphuric acid or an alkali depending on the process intent.

In operation, blended slurry received by feed tank 14 is pumped (8) into the autoclave first compartment. As the reaction proceeds and energy is released the temperature attains the set temperature for this compartment. At temperatures above the set point the slurry is discharged from the first compartment as stream (9) to the flash tank 20 where a flash component (5) is released either to atmosphere or to a heating duty elsewhere. The flash tank underflow is drained to thickener 22 where a phase separation is achieved with the aid of a flocculant stream (14). The overflow (13) is directed externally to the autoclave discharge tank 18, while the thickened solids (12) are returned to the autoclave feed tank 14. The flash thickener recycle system is referred to as "the FTR".

In the design or modification of an existing autoclave, the compartment is sized to achieve in excess of 50% typically 90 - 95% of the overall reaction extent. This ensures that the thickener 22 overflow is very similar in composition to the autoclave discharge stream (10) after flash.

The mean flow rate in the first and, in this case, ensuing compartments is not the difference of {(2) + (7) + (6)} and stream (5) as it would be in a flash recycle system, but is {(2) + (7) + (6) less [(5) + (13)]} in the

FTR. Thus the retention time can be increased by over 300%. Other factors such as oxygen gas mass transfer at the autoclave impellers may become rate limiting or alternately the feed pumps on feed tank servicing the autoclave may reach their limit and thereby constrain further productivity gains.

Existing autoclaves originally fitted with a quench cooling system can in certain cases be increased in capacity by in excess of 100% whilst, in some cases, derated in pressure and temperature by employing the flash, thickener, recycle process of the invention. The net feed rate (11) through the autoclave can be adjusted to suit the required mass flow and extraction simply by adjusting the volumetric flow at streams (12) and (13).

An example will now be given relating to the processing of nickel-copper sulphide mattes.

An autoclave system originally designed to process approximately 20 tonnes of matte per day was converted to incorporate the FTR process.

The flowsheet employed was similar to that in Figure 3. The feed rate at stream (2) consisted of a matte semi-product from a previous step in the flowsheet. The operating temperature of the first compartment was 140°C and the first pass extraction of new feed to the first compartment was typically 90%. Some of this "partially leached" feed from the first compartment was partly fed forward to the second compartment stream (11), but a majority was directed with first compartment temperature control to the flash tank where the underflow was fed to the thickener.

The thickener overflow gravitated to the autoclave discharge tank and the solids plus some liquor comprising stream (12) fed to feed tank 14.

The slurry comprising stream (11) was further leached in the second and ensuing compartments and finally discharged as stream (10) when it was flashed (15) into the discharge tank. The flash underflow and the thickener overflow (13) were blended in the discharge tank.

The chemistry in the autoclave can, in its simplified form, be represented by the following equations:

$$NiS + 4O \Longrightarrow NiSO_4$$

$$Cu_2S + H_2SO_4 + 5O \Longrightarrow 2\ CuSO_4 + H_2O$$

Both these reactions generated significant energy and between 1 and 1½ tonnes of steam per hour was released in the flash (5).

The composition of various streams is given below in tables 1A, 2A and 3A at the end of this description.

The net flow through the autoclave is calculated by difference as stream (11) without compensating for density within the autoclave.

The net flow (11) is approximately 20% of the feed flow (2). However prior to this incorporation of this invention the feed flow was 8.4 m^3/h with a mass flow of 20 tonnes matte equivalent. The solids feed with this invention was 39 tonnes of matte equivalent at 13.1 m^3/h aqueous flow.

Figure 2 shows a further example 10.2 of the invention with two FTR processes. Figure 4 is similar to the flowsheet of Figure 3 with the exception that an additional compartment stage has been added to the autoclave 16.2 and a further FTR process including flash tank 20.2, thickener 22.2 and feed tank 24 provided for flash thickening recycling between the last and second last compartments of the autoclave. This additional stage is an integral part of the same pressure envelope and has been incorporated to increase the extent by, in this case, altering the process conditions generally prevailing in the first part of the autoclave. This example is not necessarily related to a single additional stage, but may embrace more than one stage. Furthermore it may involve the return of the aqueous stream (16) to the additional stage of the autoclave as opposed to the residue fraction as shown in Figure 4.

The autoclave conditions may be changed to incorporate an "equilibrium" break by removing most of the leachate from the residue before returning it to the additional stage as shown in Figure 4. The objective may be to alter the slurry EH in the additional stage and thereby extract elements not extracted in the first four compartments of the autoclave depicted in Figure 3.

In operation, the slurry from the fourth compartment (10) is flashed in flash tank 20.2 and the underflow passes to thickener 22.2. The overflow (16) from this thickener is processed further for the recovery of copper while the underflow is pumped to the second autoclave feed tank 24 dedicated to feed the slurry after diluting in process water and sulphuric acid back to the autoclave (stream 19). The slurry reacts further in the autoclave fifth compartment before being discharged as stream (20).

In this case because the objective is one of maximizing the reaction extent, oxygen is primarily introduced into this fifth compartment and it then travels countercurrent in the autoclave head space thereby ensuring optimal conditions for achieving the specified objective.

The process conditions for this example are given in Tables 1B, 2B & 3B and reflect the effect of adding the extra stage to the autoclave.

The flash recycle processes is imminently suited to the treatment of alloys. Such alloys often contain arsenic, carbon and phosphorous and when processed in an acidic environment can yield dangerous and toxic gases such as hydrogen, arsine, phosphine and acetylene. The formation of certain of these gases such as hydrogen and arsine can be avoided if an electro-positive element, such as cupric copper, is present in the aqueous phase in an acceptable concentration and if the slurry is well mixed. However in the presence of acid and alloy, copper is often removed from solution by cementation or metathesis and once this happens these dangerous gases can form. If for example, an alloy containing copper, nickel (or cobalt) and iron were to be processed, a variant of the flowsheet of Figure 2 could be considered.

Figure 3 shows a leach process 10.3 to co-extract the value metals nickel, cobalt and copper simultaneously and reject the iron. The alloy containing these value metals may contain some carbon as carbide Fe_3C or cementite and small quantities of arsenic. In sulphuric acid media, acetylene and arsine can be produced along with hydrogen and these gases can present serious risks to personnel and to the safe operation of the process equipment employed in the leach. The value metals leave the leach as sulphates.

The flash recycle is developed in a manner that ensures the safe operation of the process equipment in the following respects:

a. process conditions can be selected in the autoclave to ensure that the returning slurry from the autoclave 16 first compartment contains very significant concentrations of copper. This is despite cementation having accounted for most of the soluble copper externally to the autoclave in, for example, a classical process not employing this massive recycle from the first compartment.

b. this soluble copper is made available to the feed tank 14 in the returning slurry thereby ensuring that the formation of any noxious gases is prevented.

c. the flash vapour from the slurry fills the head space of the feed tank 14 and sweeps any acetylene out of the vessels, prevents air ingress and generally prevents conditions favourable for an explosion to take place.

d. some of this flash steam can be directed to the density adjust tank 12 for the same duty if process conditions warrant it.

The invention is not limited to the precise details described above and shown in the drawings. Modifications may be made and other embodiments developed without departing from the spirit of the invention.

DATE 7 January 2004

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TABLE 1A

	Stream Nº	Solids Composition (%)				
		Ni	**Cu**	**Fe**	**S**	**Tie inert**
Matte Feed	(1)	28.8	54.4	2.4	22.4	0.305
Auto Feed Solids	(8)	16.9	63.4	2.7	25.8	0.787
Thickener Underflow	(12)	10.4	50.9	0.8	23.4	1.55
Fourth Compartment	(10)	6.05	43.0	1.1	21.8	4.87

TABLE 2A

	Stream Nº	Liquor Composition (g/l)			
		Ni	**Cu**	**Fe**	**H_2SO_4**
Spent Electrolyte	(4)	48	25	1.5	77
Slurry Feed	(2)	40	24	1.2	49
Autoclave Feed	(8)	57	64	1.6	49
Flash Feed	(9)	63	85	1.7	18
Thickener Overflow	(13)	63	85	1.7	18
Fourth Compartment	(10)	58	112	1.3	15

TABLE 3A

	Steam Nº	Flow (m^3/h)		Steam Nº	Flow (m^3/h)
Slurry Feed	(2)	12.9	Flash Equivalent Flow	(5)	2.7
Process Water	(7)	0.4	Thickener Overflow	(13)	8.0
Sulphuric Acid	(6)	0.24	Autoclave Flow	(11)	2.6
Total aqueous flow		13.3	Total aqueous flow		13.3

TABLE 1B

	Stream Nº	Solids Composition (%)				
		Ni	**Cu**	**Fe**	**S**	**Tie inert**
Matte Feed	(1)	28.8	54.4	2.4	22.4	0.305
Auto Feed Solids	(8)	16.9	63.4	2.7	25.8	0.787
Thickener Underflow	(12)	10.4	50.9	0.8	23.4	1.55
Fourth Compartment	(10)	6.05	43	1.1	21.8	4.87
Fifth Compartment	(20)	2.8	1.2	1.6	7	32.5

TABLE 2B

	Stream Nº	Liquor Composition (g/l)			
		Ni	**Cu**	**Fe**	**H_2SO_4**
Spent Electrolyte	(4)	48	25	1.5	77
Slurry Feed	(2)	40	24	1.2	49
Autoclave Feed	(8)	57	64	1.6	49
Flash Feed	(9)	63	85	1.7	18
Thickener Overflow	(13)	63	85	1.7	18
Fourth Compartment	(10)	58	112	1.3	15
Fifth Compartment	(20)	8	44	0.8	42

TABLE 3B

	Steam Nº	Flow (m^3/h)		Steam Nº	Flow (m^3/h)
Slurry Feed	(2)	12.9	Flash Equivalent Flow	(5)	2.7
Process Water	(7)	0.4	Thickener Overflow	(13)	8.0
Sulphuric Acid	(6)	0.24	Autoclave Flow	(11)	2.6
Process Water	(17)	0.9			
Sulphuric Acid	(18)	0.03	Slurry Discharge	(20)	1.2
Slurry Feed	(19)	1.2			

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~~Figure 3~~

FLASH THICKENER RECYCLE (FTR)
PROCESS

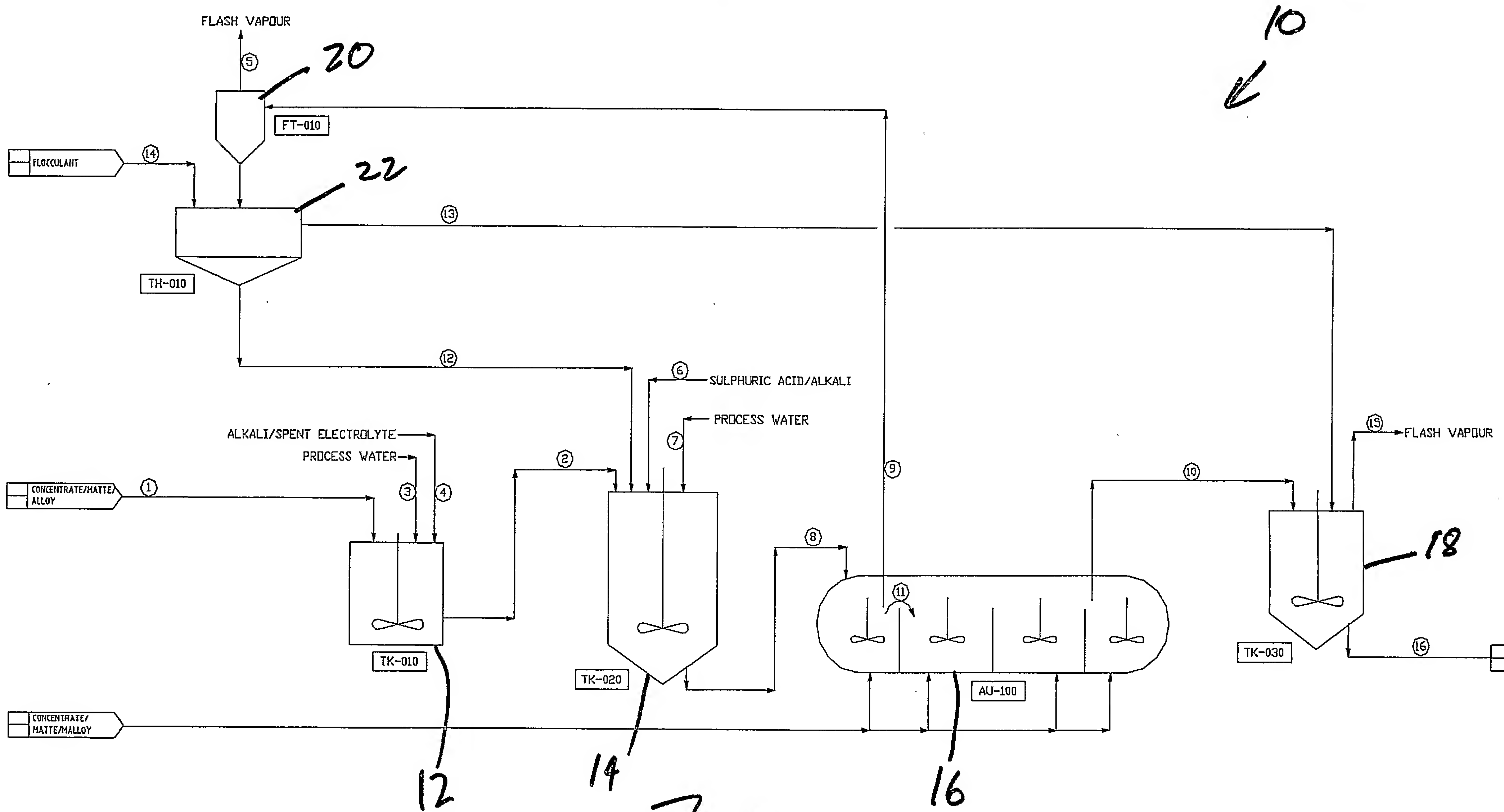

Fig I

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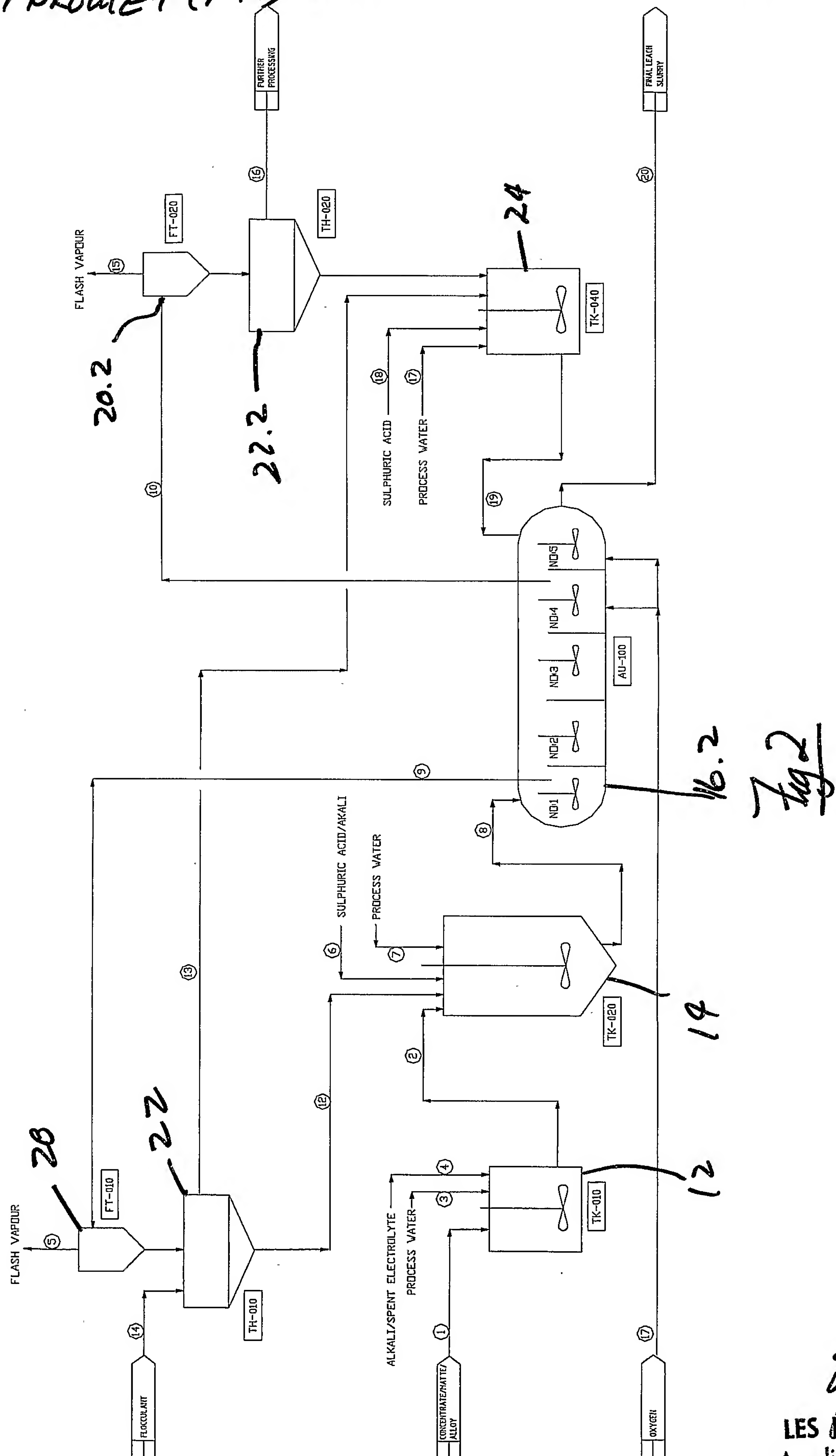
• • 2004 / 0082 2/3

Figure 4

FLASH THICKENER RECYCLE (FTR) PROCESS



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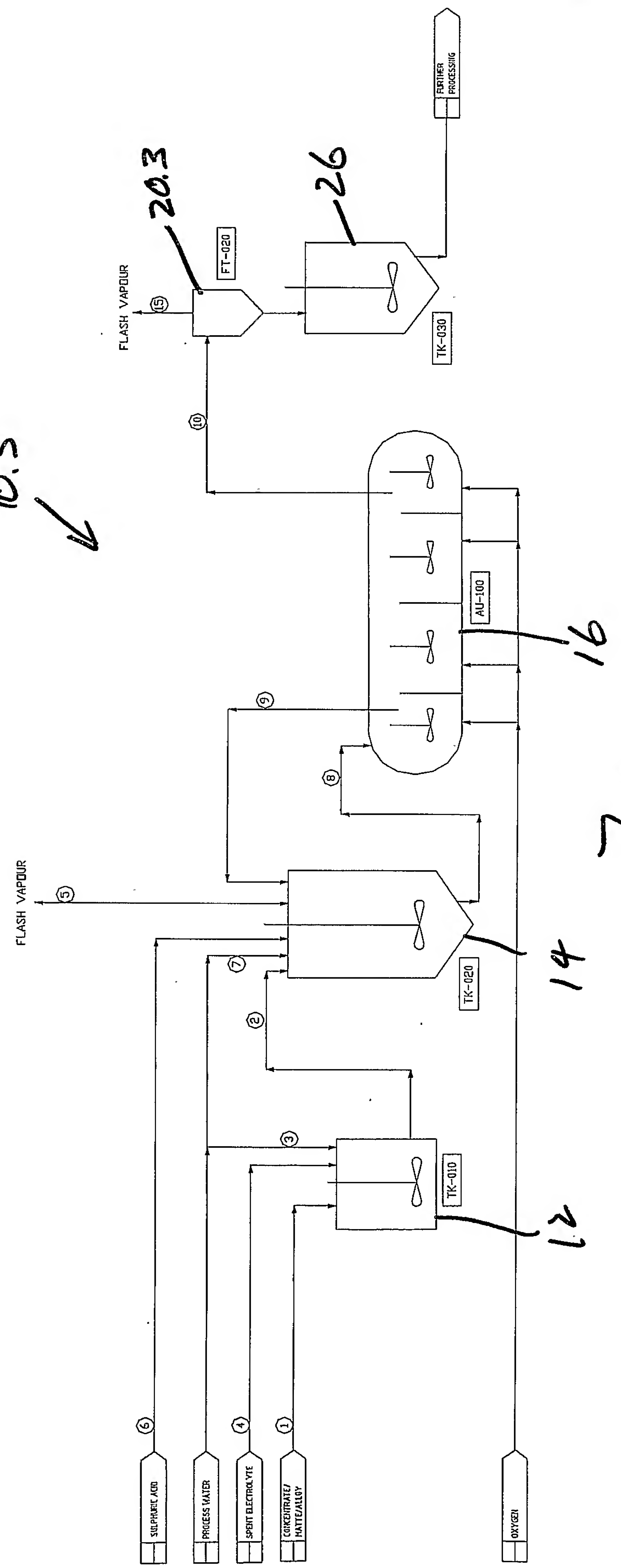
2004/0082

3/3

Figure 5

FLASH RECYCLE (FR)
FLOWSHEET
FOR THE LEACH OF ALLOYS



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